

Memorandum 4166

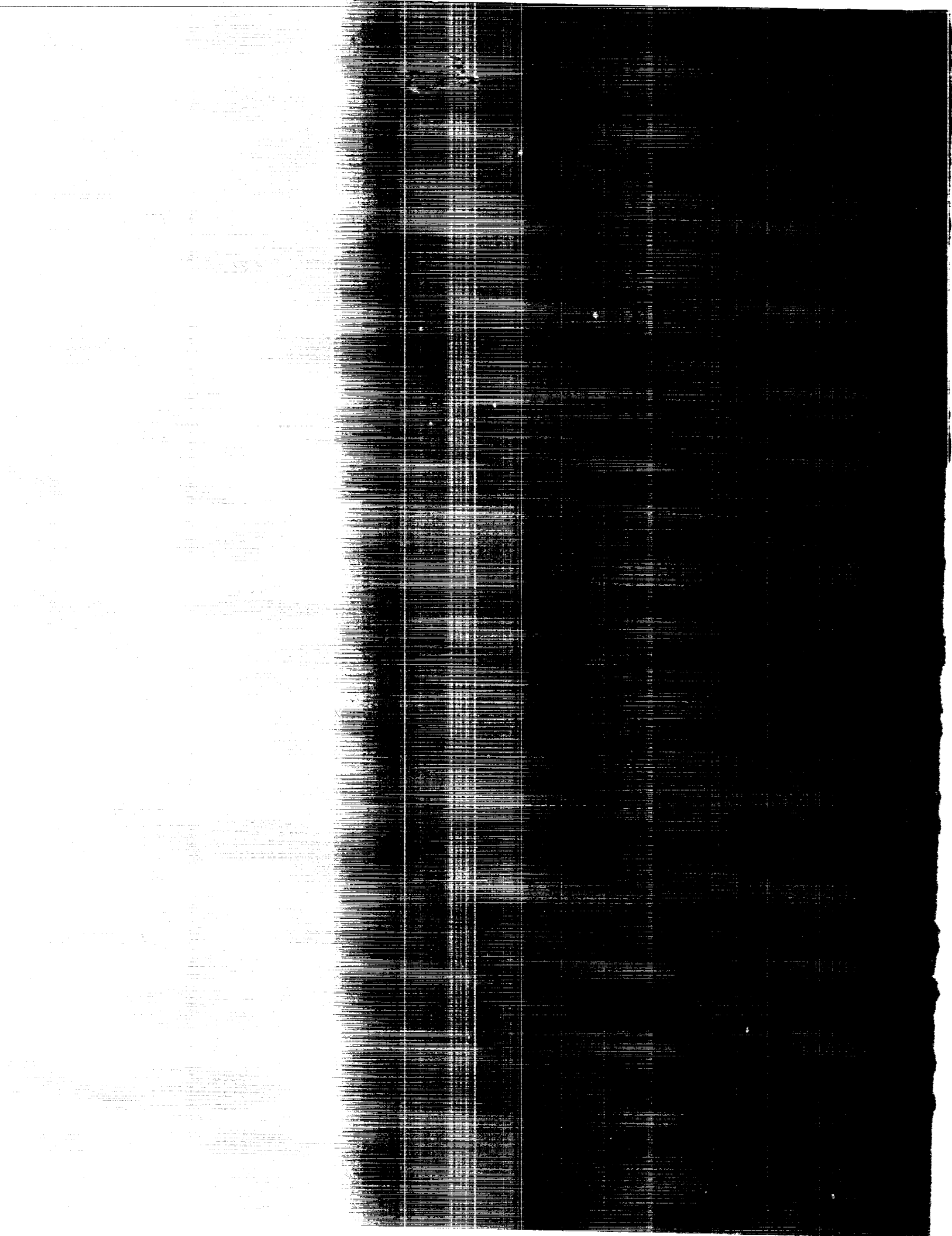
Initiators and
Laser-Induced
Copolymerization of Styrene
and Maleic Anhydride in Acetone

J. E. Meador,

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Initiation Precursors and
Initiators in Laser-Induced
Copolymerization of Styrene
and Maleic Anhydride in Acetone

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Abstract

The initiation step of photopolymerized styrene/maleic anhydride copolymer was investigated at 365 nm using an ultraviolet-visible spectrophotometer. The ultraviolet absorption measurements provide decisive evidence that the styrene/maleic anhydride charge-transfer complex is the sole absorbing species; however, laser experiments of this paper suggest intermediate reactions lead to a monoradical initiating species. A mechanism for the photoinitiation step of the copolymer is proposed.

Introduction

This work was part of a project in the Laser Polymerization Program in the High Energy Science Branch, Space Systems Division. The Laser Polymerization Program is part of a large program that investigates applications for lasers and the feasibility of converting laser light into heat and electrical energy. The advantage of using a laser to initiate polymerization is that it offers better control of the initiation rate and the number of free radicals produced by controlling the intensity and wavelength of the beam and the duration of irradiation.

The styrene/maleic anhydride copolymer system was chosen because it could be photo-initiated directly without the use of photosensitizers, thereby avoiding chemical contamination by initiator residues. Styrene and maleic anhydride monomers form a regularly alternating copolymer over wide ranges of mixing ratios. This phenomenon has intrigued polymer chemists for many years, and the exact mechanisms for the initiation and propagation steps are still being debated (refs. 1 and 2). Most investigations have dealt with the propagation process of thermally induced copolymers; however, attention is now being turned toward photoinitiation.

In solution styrene (Sty) and maleic anhydride (MA) form charge-transfer complexes (also known as electron donor-acceptor complexes). A charge-transfer complex (CTC) is a "rapid and reversible interaction between two molecules in solution" (ref. 3). This interaction is detectable in the ultraviolet (UV) and visible absorption spectrum for most complexes. The new absorption band due to complex formation is at wavelengths longer than the absorption bands of the individual components. Knowing that styrene and maleic anhydride form charge-transfer complexes, the question arises: What role, if any, do these complexes play in photoinitiation, propagation, and termination of the copolymer?

Recently, two groups have looked at the role of CTC's in photoinitiation and propagation of styrene/maleic anhydride copolymers using UV

lasers or monochromatic light and have proposed initiation scenarios (refs. 4 and 5). We feel both scenarios are inadequate in light of recent data from our research. The purpose of this paper is to attempt to answer some key questions concerning the role of the CTC's in the preinitiating and initiating steps through interpretation of these data.

Existing Initiation Scenarios

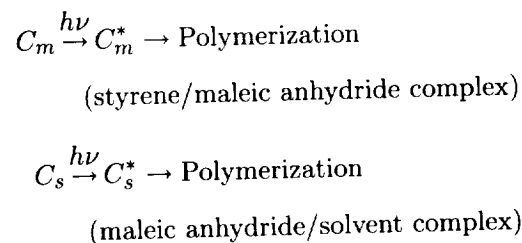
Excited Complex Mechanism

Barton et al. (ref. 4) performed absorption and rate studies on the styrene/maleic anhydride system in various solvents with a monochromatic light source at 365 nm. Two of the experiments were used to identify the initiating species: absorbance versus mole fraction of the solute of MA (x_{MA}) and rate of polymerization versus x_{MA} .

From the absorption experiments, Barton et al. observed an absorbance maximum at $x_{MA} = 0.5$ for the styrene/maleic anhydride complex (C_m) in acetone, acetonitrile, and chloroform, indicating the formation of a 1:1 complex in these solutions. In *N,N*-dimethylformamide the maximum absorption occurred at $x_{MA} = 0.6$.

They also performed rate of polymerization experiments in these solvents while varying the mole fraction of maleic anhydride. In chloroform the maximum rate of polymerization occurred at $x_{MA} = 0.5$. However, in the polar, electron-donating solvents acetone and acetonitrile, the maximum occurred at $x_{MA} = 0.8$ and 0.9, respectively.

From these results, Barton et al. suggested that in electron-donating solvents the MA/solvent complex (C_s) also absorbs photons and enters into the initiation step. They proposed the following scheme:



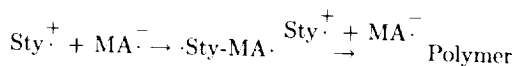
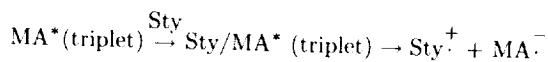
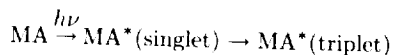
where $h\nu$ represents the absorption of a light quantum and C_m^* and C_s^* represent excited states. They also suggested that C_m^* and C_s^* may yield bipolar electron donor-acceptor products ($^+D - A^-$), diradicals ($\cdot D - A \cdot$), or ion radicals ($\cdot D^+$ and $A^- \cdot$)—all of which can initiate polymerization of ionic or radical character—but offered no evidence to support this claim.

Radical Ion Mechanism

Sadhir et al. (ref. 5) performed bulk and solution polymerizations of styrene with maleic anhydride using a Coherent Radiation CR-18 argon ion laser operating at 363.8 nm. In their bulk polymerizations, Sadhir et al. increased the molar concentration of maleic anhydride while decreasing the irradiation time of the laser. As the rate of maleic anhydride addition increased, the percent yield of the polymer increased. From these results, Sadhir et al. concluded that maleic anhydride was the absorbing species.

In their solvent experiments Sadhir et al. ran the polymerizations under similar conditions in methylene chloride, *N,N*-dimethylformamide, and toluene. The copolymer yield increased with increased solvent polarity, which suggested to them that the polymerization proceeded through a CTC.

Their absorption studies did not locate a Sty/MA absorption band; however, a MA/tetrahydrofuran absorption band (maximum at 448 nm) was detected after the solution was irradiated with an argon ion laser operating in the UV mode. From the previous polymerization experiments and this absorption measurement, Sadhir et al. proposed an initiation mechanism: Excitation of maleic anhydride occurs when a photon is absorbed. The excited MA in the singlet state crosses over into the triplet state and interacts with Sty in the ground state, forming a Sty/MA exciplex. The exciplex decomposes into ionic radicals, then combines to form diradicals to initiate polymerization:



Experimental Procedures

Laser Sources

The lasers used in these experiments were a Coherent Innova 100 20-W, continuous wave, argon ion laser and a pulsed Candela dye laser. The argon ion was operated in the UV mode at the 363.8-nm line at 0.75 W power output. The pulsed Candela laser was operated at the 365-nm line with 85 mJ energy output in a 1-ns pulse length.

Purification of Monomers

Styrene and maleic anhydride were obtained from Aldrich Chemical Company, Inc. Styrene was washed

with a 10-percent NaOH solution to remove the inhibitor, rinsed with deionized water until slightly acidic when tested with litmus paper, dried over anhydrous calcium sulfate, and vacuum distilled. Maleic anhydride was sublimed at 52°C. The solvent, acetone, was dried over potassium carbonate and distilled from potassium permanganate.

Absorption Measurements

Absorption spectra were obtained on a Perkin-Elmer Lambda 9 ultraviolet-visible-near infrared spectrophotometer for 0.1 mol·L⁻¹ MA, 0.1 mol·L⁻¹ Sty, and a 0.1 mol·L⁻¹ Sty/0.1 mol·L⁻¹ MA solution with acetone as the solvent. Pure acetone was used as the reference. Molar absorptivity measurements were made using a Beckman DU-7 UV-VIS spectrophotometer with 0.5 mol·L⁻¹ Sty/MA in acetone; acetone was used as the reference. The absorption as a function of the mole fraction of MA and the absorptivity as a function of the square of monomer concentration were determined using a Hitachi Perkin-Elmer UV-VIS spectrophotometer.

Conductivity Measurements

The conductivity of a 3 mol·L⁻¹ Sty/MA monomer solution in acetone was measured using a Horizon Ecology Company conductivity instrument (Model 1484) before and during irradiation with the argon ion laser operating at 363.8 nm and 0.75 W for a period of 3 hours. The conductivity of the solution remained at 1.45 ± 0.06 microsiemens/cm.

Results and Discussion

Spectral Measurements

Figure 1 shows absorbance in MA in acetone and equal concentrations of Sty and MA in acetone as functions of wavelength. Individually, Sty and MA absorb below 300 nm (refs. 6 and 7). The shift to longer wavelengths of the absorption bands (as compared to the absorption bands of the individual components) suggests that MA forms complexes with acetone and styrene. The formation of these complexes is well known (ref. 3); however, UV spectra for these complexes have not been published.

Since bonds are not formed between components of a CTC, the shift in the absorbance must result from the weakening of a bond within one of these complexes. From the similarity of the two spectra in figure 1, it can be concluded that MA does the absorbing within the complexes because it is the only molecule common to the two spectra. Furthermore, the bond in the MA that does the absorbing is the carbon-carbon double bond. This follows from the susceptibility of the π -electrons to outside influences and because it is the bond broken in the polymer

formation. A case can be made that the weakening of the carbon-carbon double bond is greater for the complex formed in the Sty/MA/acetone solution than for the MA/acetone complex because the Sty/MA/acetone solution absorbs at longer wavelengths (lower energies).

Even though most of the Sty/MA/acetone absorption band overlaps with the MA/acetone complex absorption band, at wavelengths above 360 nm only the Sty/MA/acetone solution is absorbing. Not only does this enable identification of the initiating precursor, it makes initiation of the polymer possible with an argon ion laser.

Table I provides the measured molar absorptivity values of each species at 365 nm. This provides for a quantitative interpretation of figure 1 at 365 nm. However, the absorbing complex is not identified by either figure 1 or the measurements of table I. It is surmised to be the Sty/MA complex, but it could be a complex between all the components in the solution. A Sty/acetone complex was ruled out by the Sty/acetone absorptivity measurement and the fact that both Sty and acetone are donor molecules. Further measurements are needed to confirm this absorption as the Sty/MA complex absorption.

Figure 2 shows the absorptivity of the solution as a function of the square of the monomer concentration M . From Beer's law

$$dI = -\beta I C_m ds \quad (1)$$

$$\frac{I_o}{I} = e^{\beta C_m s} \quad (2)$$

$$\frac{dC_m}{dt} = kM_1M_2 - k'C_m \rightarrow C_m \propto M_1M_2 \quad (3)$$

$$10 \log \frac{I_o}{I} \propto C_m \propto M_1M_2 = (M - M_1)M\gamma \\ = M^2\gamma(1 - \gamma) \quad (4)$$

where I_o represents the radiation intensity before it passes through the solution, I is the radiation intensity after it passes through the solution, β is the absorptivity of the solution, s is path length, k and k' are rate coefficients, $M = M_1 + M_2$, $M_1 = [\text{Sty}]$, $M_2 = [\text{MA}]$, and $\gamma = [\text{MA}]/([\text{Sty}] + [\text{MA}])$. Therefore, if $10 \log(I_o/I)$ versus M^2 is linear, then the absorbing species is C_m . Figure 2 verifies that C_m is the absorbing species because a linear relationship is observed.

Figure 3 is a repeat of the absorption measurement by Barton et al. for the Sty/MA/acetone solution. The absorbance of the solution is plotted as a function of the solute mole fraction of MA. The maximum at $x_{\text{MA}} = 0.5$ also verifies C_m as the absorbing

species (also from eq. (4)) and confirms the Sty/MA complex ratio as 1:1.

These absorption measurements establish C_m as the sole absorbing species. With this lone absorption measurement, Barton et al. were not able to rule out C_s as an absorbing species solvent. The complex C_s was concluded to be an initiating precursor because a shift to higher MA mole fractions for the rate of polymerization as compared with the 0.5 MA mole fraction in the absorption measurement was observed. However, if C_s does not absorb at 365 nm in the absorption measurements, it will not absorb at 365 nm during the polymerization experiments either. More than likely, since MA complexes with the solvent, the available free MA is removed from the solution pool and greater concentrations of MA are required to achieve the maximum C_m concentration—hence the shift in the mole fraction of MA to achieve the maximum rate of polymerization.

For whatever reasons, Sadhir et al. did not observe a Sty/MA complex absorption band, but they did observe an absorption band after irradiating a solution of maleic anhydride in tetrahydrofuran with an argon ion laser. From this experiment and the knowledge that MA forms strong CTC's with tetrahydrofuran and dioxane, Sadhir et al. proposed that MA was the initiation species. This seems unlikely since pure MA absorbs at wavelengths much lower than 365 nm.

Clearly, the C_m is the absorbing species or initiator precursor at 365 nm. What the initiating species are and by what mechanisms the initiator precursors become the initiating species are questions not as easily answered. The following two experiments offered insights into these questions.

Radical Characterization

A combined 5 mol·L⁻¹ Sty/MA monomer solution in acetone in a 1 × 1 × 3.5 cm quartz cell at room temperature was irradiated with a Candela dye laser operating at 365 nm, 60 Hz, 1 ns/pulse, and 85 mJ/pulse. Samples were irradiated for periods of 30 min, 45 min, and 60 min. No copolymer was obtained.

In a reaction, a description of the system is based on the probability of a number of events occurring in a given time in a given volume. Three major types of reactions are occurring: initiation of radicals, propagation of polymer chains, and termination of these chains. Given a source of radicals, the outcome of a polymer reaction is based on two equations:

$$\text{Propagation} = \sigma_p [R][M] \quad (5)$$

$$\text{Termination} = \sigma_t [R]^2 \quad (6)$$

where σ_p is the propagation cross section, σ_t is the termination cross section, $[R]$ is the concentration of radicals, and $[M]$ is the concentration of monomers. Since σ_t is much greater than σ_p , in order to obtain polymer, $[R]$ must be kept small or termination will become the dominant reaction.

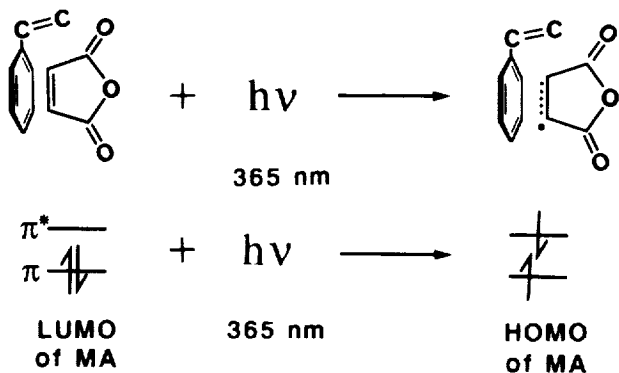
These data suggest that radicals terminate before they grow polymer chains. This could not happen if diradicals were formed because collisions would not result in termination. The only mechanism that can explain this result is the formation of monoradicals.

Pulsed lasers deposit large quantities of photons in a short period of time, resulting in a large number of monoradicals being formed. The use of a pulsed laser in this system is equivalent to adding a large quantity of peroxide initiator in a thermal polymerization. No polymer would form; at best, oligomers would form. Therefore, another mechanism must occur between the absorption of the photon and the initiation of the polymer that produces a monoradical.

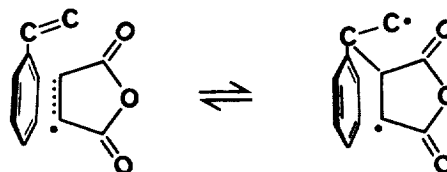
The second experiment to provide insight into the initiating species was the conductivity experiment. In this experiment, the conductivity of the solution remained constant throughout irradiation, indicating that radical ions and ion species were not being formed. This eliminates the bipolar electron donor-acceptor products, diradicals, and ion radicals as possible initiating species suggested by Barton et al. and Sadhir et al.

Proposed Scenario

The proximity of Sty to MA weakens the carbon-carbon double bond in MA. This weakening is a result of an overlap between the highest occupied molecular orbital (HOMO) of the styrene and the lowest unoccupied molecular orbital (LUMO) of the maleic anhydride. This results in a shift of the individual absorption bands to an absorption band at longer wavelengths by C_m . It also allows the absorption of a photon at 365 nm. When a photon is absorbed, a π -electron from MA is promoted to the antibonding π^* molecular orbital, as shown below.

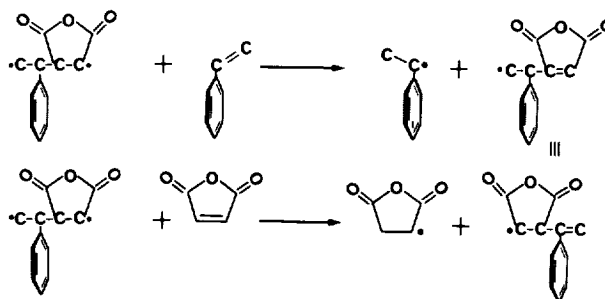


Once the photon has been absorbed, two things can happen. Either absorbed energy from the photon is released through fluorescence and C_m returns to the ground state or C_m is transformed into the diradical and thus survives. But this diradical does not initiate polymerization. Another mechanism occurs to produce a monoradical that initiates the copolymer.



Unlike the model of Sadhir et al., the above transition is a very probable and natural transition. Sadhir et al. suggest that once the MA absorbs the photon, an excited singlet state is created that crosses over into the metastable triplet state. For this to happen, a perturbation of some type must occur. Sadhir et al. show no perturbation occurring.

Knowing from the pulsed laser experiment and the conductivity experiments that diradicals and ionic species are not involved, some other type of mechanism must be generating the monoradical. A possibility that neither Barton et al. nor Sadhir et al. suggest is a mechanism similar to the mechanism proposed for the radical polymerization of polystyrene (refs. 8 and 9). Once the diradical has formed, the diradical can interact with either a Sty molecule or a MA molecule, yielding two monoradicals as diagrammed below. These monoradicals can then initiate the polymerization.



Conclusions

At 365 nm, the initiating precursor in a styrene/maleic anhydride/acetone solution is the styrene/maleic anhydride complex. The perturbation of the

styrene allows the weakening of the maleic anhydride vinyl bond and absorption of a photon at that energy. A diradical is then formed, and the diradical reacts with a ground state styrene or maleic anhydride molecule to form two monoradicals. The present analysis suggests that these monoradicals are the species that initiate the copolymerization.

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Table I. Absorptivity Measurements at 365 nm

Measurements were made at 22°C with a monomer concentration of $M = 0.5$ in acetone; pure acetone was used as the reference

Species	Molar absorptivity, ϵ , [†] $\text{L}\cdot\text{cm}^{-1}\cdot\text{mol}^{-1}$
Styrene	0.0095
Maleic anhydride	.0145
Styrene/maleic anhydride	.4188

[†] $\epsilon = \frac{A}{bc}$ where A is the absorbance of the solution, b is the path length in cm, and c is the concentration in mol/L.

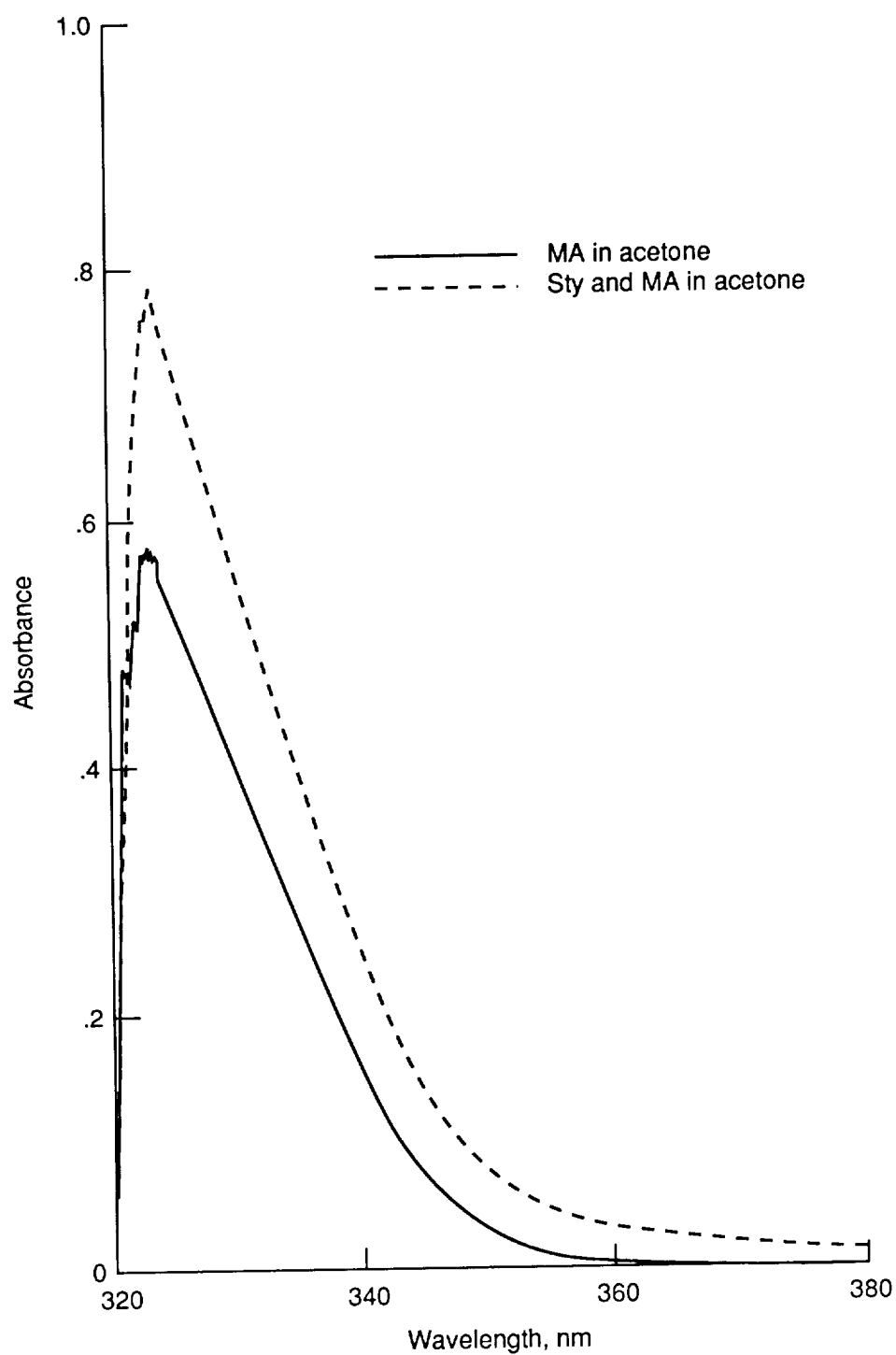


Figure 1. Absorbance versus wavelength of $0.1 \text{ mol}\cdot\text{L}^{-1}$ MA in acetone and $0.1 \text{ mol}\cdot\text{L}^{-1}$ Sty and $0.1 \text{ mol}\cdot\text{L}^{-1}$ MA in acetone.

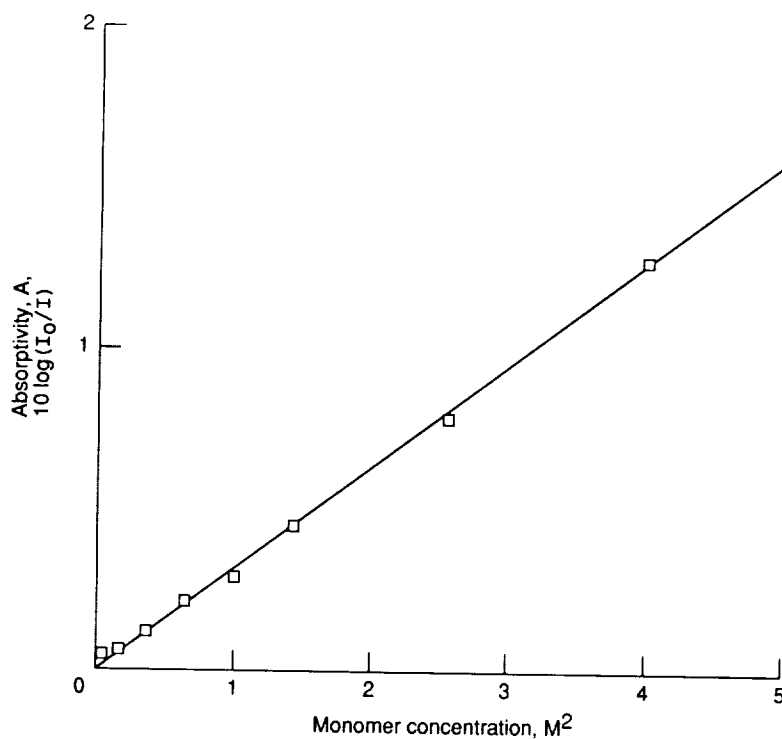


Figure 2. Absorptivity versus M^2 . Ultraviolet-visible spectrophotometric measurements at 365 nm; 1-cm path length; total monomer concentration varied from 0.1 to 1 mol·L⁻¹; I_0 normalized to the absorbance of acetone.

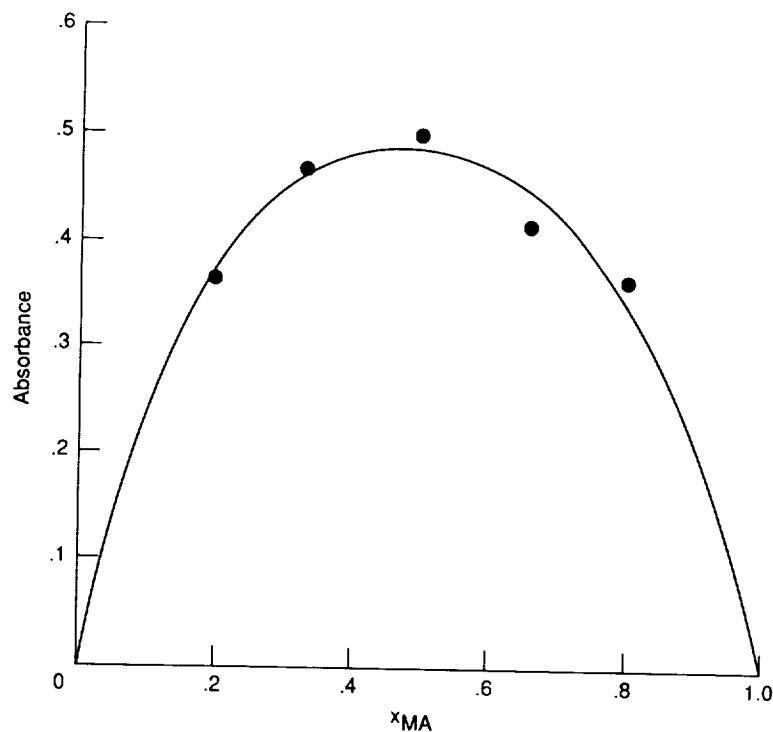


Figure 3. Absorbance versus mole fraction. Absorbance = $-\log(I/I_0)$; measurements at 365 nm; 1-cm path length; total monomer concentration 1 mol·L⁻¹; I_0 normalized to the absorbance of acetone.



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